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Publication number: **0 317 106 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(43) Date of publication of patent specification: 17.02.93 (51) Int. Cl.⁵: C08J 3/03, C08J 3/24

(21) Application number: 88310157.8

(22) Date of filing: 28.10.88

(54) Method of surface-treating water-absorbent resin.

(30) Priority: 29.10.87 JP 271798/87

(43) Date of publication of application:
24.05.89 Bulletin 89/21

(45) Publication of the grant of the patent:
17.02.93 Bulletin 93/07

(54) Designated Contracting States:
BE CH DE ES FR GB IT LI NL SE

(56) References cited:
EP-A- 0 233 014
FR-A- 2 559 158
GB-A- 2 126 591

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It is an object of this invention therefore to provide a water-absorbent resin having well-balanced excellent properties such as a high absorbancy or a high rate of absorption upon contact with an aqueous liquid and a high liquid drawing force by discovering a method of uniformly and efficiently crosslinking the surface of the water-absorbent resin.

In order to achieve the above object, we made extensive investigations, and have now found that the surface of a water-absorbent resin can be uniformly and efficiently crosslinked by adding a dispersion of a hydrophilic crosslinking agent obtained by dispersing the hydrophilic crosslinking agent in a hydrophobic organic solvent in the presence of a surface-active agent to a suspension of the water-absorbent resin in a hydrophobic organic solvent.

Thus, according to this invention, there is provided a method of treating the surface of a water-absorbent resin which comprises adding a hydrophilic crosslinking agent capable of reacting with at least two functional groups of the water-absorbent resin to a suspension of the water-absorbent resin in a hydrophobic organic solvent to crosslink the surface and its vicinity of the resin, wherein the hydrophilic crosslinking agent is added in the form of a dispersion obtained by dispersing it in a hydrophobic organic solvent in the presence of a surface-active agent.

The water-absorbent resin to be surface-treated by this invention is a resin which contains functional groups such as carboxyl, sulfonic acid and amino groups, and in water, absorbs a large amount of water and swells to form a hydrogel. Examples of the water-absorbent resin include a hydrolyzate of a starch/acrylonitrile graft copolymer, a neutralization product of a starch/acrylic acid graft copolymer, a saponification product of an acrylate/vinyl acetate copolymer, a hydrolyzate of an acrylonitrile copolymer or an acrylamide copolymer, a modification product of crosslinked polyvinyl alcohol, a neutralization product of self-crosslinking polyacrylic acid, a crosslinked polyacrylate salt, and a neutralization product of a crosslinked isobutylene/maleic anhydride copolymer.

These water-absorbent resins can generally be obtained by polymerizing water-soluble ethylenically unsaturated monomers.

The water-absorbent resins used in this invention can be obtained by using monomers having functional groups as essential components. Examples of the monomers having functional groups include anionic monomers and their salts, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, 2-(meth)acryloylethanesulfonic acid, 2-(meth)acryloylpropanesulfonic acid, 2-(meth)acrylamide-2-methylpropanesulfonic acid, vinylsulfonic acid and styrenesulfonic acid; and cationic monomers or their quaternized products with mineral acids, such as diethylaminoethyl (meth)acrylate, diethylaminopropyl (meth)acrylate and dimethylaminopropyl (meth)acrylamide. One or more of these monomers can be used. It is preferred to use acrylic acid, methacrylic acid, and their salts as essential main components. As required, other monomers may be used in combination with the above monomers containing functional groups. The other monomers that can be used are, for example, monomers containing nonionic hydrophilic groups, such as (meth)acrylamide, N-substituted (meth)acrylamide, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate.

Water-absorbent resins obtained by copolymerizing a very small amount of a crosslinking agent having polymerizable unsaturated groups or reactive functional groups are preferred to self-crosslinking water-absorbent resins without a crosslinking agent.

Examples of the crosslinking agent include N,N'-methylenebis(meth)acrylamide, N-methylol (meth)acrylamide, (poly)ethylene glycol di(meth)acrylate, (poly)propylene glycol di(meth)acrylate, glycerol tri(meth)acrylate, glycerol di(meth)acrylate, polyvalent metal salts of (meth)acrylic acid, trimethylolpropane tri(meth)acrylate, triallylamine, triallyl cyanurate, triallyl isocyanurate, triallyl phosphate, glycidyl (meth)acrylate, ethylene glycol diglycidyl ether, glycerol tri(di)glycidyl ether, and polyethylene glycol diglycidyl ether. Two or more of these crosslinking agents may be used in combination. The amount of the crosslinking agent used is generally about 0.001 mole % to 1.0 mole % based on the water-soluble ethylenically unsaturated monomers.

The water-absorbent resins may be obtained by using various polymerization methods such as aqueous polymerization, inverse-phase suspension polymerization, precipitation polymerization and bulk polymerization. The aqueous solution polymerization or the inverse-phase suspension polymerization method are preferred from the standpoint of operability during polymerization and handability during the surface-treatment of the water-absorbent resins. The inverse-phase suspension polymerization method is especially preferred in view of the dispersibility of the water-absorbent resin in a hydrophobic organic solvent.

The concentration of the monomers in the aqueous solution of the monomers in the production of water-absorbent resins by aqueous solution polymerization or inverse-phase suspension polymerization may be varied over a wide range. Generally, it is at least 25 % by weight, preferably at least 35 % by weight, to a saturation concentration.

The surface-active agent used in obtaining the dispersion of the hydrophilic crosslinking agent may be at least one member selected from nonionic surface-active agents, anionic surface-active agents, cationic surface-active agents, amphoteric surface-active agents, and polymeric surface-active agents. Examples of the non-ionic surface active agents are sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, glycerol or polyglycerol fatty acid esters, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxyethylene acyl esters and sucrose fatty acid esters. Examples of the anionic surface-active agents include higher alcohol sulfates, alkylnaphthalenesulfonates, alkylpolyoxyethylenesulfates and dialkylsulfosuccinates. Examples of the cationic surface-active agents are alkyl quaternary ammonium salts and alkylamine salts. Examples of the amphoteric surface-active agents are alkylbetains and lecithin. Examples of the polymeric surface-active agents are oleophilic polymers having carboxyl groups. Of these, nonionic surface-active agents having an HLB of at least 3 or anionic surface-active agents are preferred.

The suitable amount of the surface-active agent used is 0.001 to 0.5 part by weight per part by weight of the hydrophobic organic solvent. If it is less than 0.0001 part by weight, it is difficult to achieve a uniform crosslinking treatment of the surface of the water-absorbent resin with the hydrophilic crosslinking agent, and the final water-absorbent resin obtained tends to show an insufficient improving effect in properties. If it is larger than 0.5 part by weight, no corresponding increase in properties can be obtained.

If desired, part of the surface-active agent may be incorporated in the hydrophobic organic solvent used to suspend the water-absorbent resin.

The dispersion of the hydrophilic crosslinking agent may be prepared by any method by which the hydrophilic crosslinking agent can be stably dispersed in the hydrophobic organic solvent by the surface-active agent, for example by adding the hydrophilic crosslinking agent to the optionally heated hydrophobic organic solvent containing the surface-active agent with intense stirring or shaking, or by adding the surface-active agent to a mixture of the hydrophilic crosslinking agent and the hydrophobic organic solvent with intense stirring or shaking.

In the present invention, the dispersion of the hydrophilic crosslinking agent denotes an emulsion or suspension in which the hydrophilic crosslinking agent, or its solution in water or a water-soluble organic solvent is dispersed as fine liquid droplets in the hydrophobic organic solvent. The average liquid droplet size of the dispersion of the hydrophilic crosslinking agent may vary widely depending upon the particle diameter of the water-absorbent resin, and may usually be within the range of 0.01 to 100 micrometers. To achieve a uniform surface-treatment, the average liquid droplet size is preferably small, for example 0.01 to 50 micrometers. A dispersion having an average liquid droplet size of less than 0.01 micrometer is difficult to obtain with an ordinary stirrer, and a special stirrer is required.

In the method of this invention, the addition of the dispersion of the hydrophilic crosslinking agent to the suspension of the water-absorbent resin may be effected by any method, for example by adding the dispersion of the hydrophilic crosslinking agent to the suspension of the water-absorbent resin with stirring.

To crosslink the surface and its vicinity of the water-absorbent resin with the hydrophilic crosslinking agent, the water-absorbent resin is maintained at the reaction temperature determined according to the type of the hydrophilic crosslinking agent obtained. For example, it can be accomplished by maintaining the suspension of the water-absorbent resin mixed with the dispersion of the hydrophilic crosslinking agent at a temperature of usually 10 to 250 °C, preferably 50 to 180 °C to effect crosslinking reaction, or by separating the water-absorbent resin from the suspension of the water-absorbent resin mixed with the dispersion of the hydrophilic crosslinking agent by filtration or the like and then heat-treating the separated resin in an ordinary dryer or a heating oven.

If the water-absorbent resin is obtained by aqueous solution polymerization or inverse-phase suspension polymerization, it is difficult to remove water used at the time of polymerization completely. However, according to the method of this invention, water-absorbent resins having a water content of 5 to 25 % by weight can be used as the starting material.

According to the method of this invention by which the surface and its vicinity of the water-absorbent resin is crosslinked by adding the dispersion of the hydrophilic crosslinking agent, which is obtained by dispersing it in the hydrophobic organic solvent in the presence of the surface-active agent, to the suspension of the water-absorbent resin in the hydrophobic organic solvent, a uniform crosslinked layer can be formed on the surface of the water-absorbent resin, and the properties of the surface of the water-absorbent resin can be improved so as to adapt them favorably to a water-absorbing material.

Accordingly, the water-absorbent resin surface-treated by the method of this invention has a high absorbancy and a high rate of absorption upon contact with an aqueous liquid, and an excellent force of drawing liquid from a substrate containing an aqueous liquid.

Furthermore, the method of this invention is industrially advantageous in that since it does not use a hydrophilic organic solvent, the hydrophobic organic solvent used in this invention can be easily separated

dispersion of the hydrophilic crosslinking agent in Example 1. The properties of these water-absorbent resins (2) to (4) were examined, and the results are shown in Table 2.

Table 1

Example	Surface-treated water-absorbent resin	Surface-active agent used		Average liquid droplet diameter (micrometers) of the dispersion of the cross-linking agent
		Type (*)	Amount (g)	
2	(2)	Sorbitan mono-stearate	0.3	15
3	(3)	Polyoxyethylene sorbitan mono-stearate	0.4	3
4	(4)	Sodium dialkyl-sulfosuccinate	0.5	0.9

(*) These surface-active agents are commercially available from Kao Co., Ltd. under the following tradenames.

Sorbitan monostearate (Rheodol SP-S10, HLB=4.7).

Polyoxyethylene sorbitan monostearate (Rheodol TW-S120, HLB=14.9).

Sodium dialkylsulfosuccinate (Pelex OT-P).

EXAMPLE 5

The same polymerization as in Example 1 was carried out except that 1.5 g of ethyl cellulose was used instead of 2.0 g of sorbitan monostearate as the dispersing agent during polymerization. After the polymerization, most of water was evaporated by azeotropic dehydration to give a cyclohexane suspension of the polymer. The resulting polymer had a water content of 17 %.

Separately, a solution of 0.04 g of ethylene glycol diglycidyl ether in 2 ml of water and 20 g of cyclohexane were introduced into a flask. A solution of 0.5 g of polyoxyethylene cetyl ether (Emulgen 220, a product of Kao Co., Ltd.; HLB=14.2) in 10 g of cyclohexane was added with strong stirring to give a dispersion of ethylene glycol diglycidyl ether. The dispersion had an average liquid droplet diameter of 5 micrometers.

The dispersion was added with stirring to the polymer suspension at room temperature. The mixture was heated to 75 °C, and maintained at this temperature for 3 hours.

Cyclohexane was then removed by filtration, and the resulting solid was dried under reduced pressure at 80 °C to obtain a surface-treated water-absorbent resin (5).

Table 2

	Water-absorbent resin	Properties of the water-absorbent resin				
		Absorbancy (g/g)		Rate absorption (sec)	Drawing force (g)	Formation of an undissolved powder lump
		3 minutes later	30 minutes later			
Example	1	43	57	40	16.4	No
	2	46	56	36	17.0	"
	3	45	58	34	16.7	"
	4	43	52	29	17.2	"
	5	41	58	29	17.6	"
	6	48	57	41	15.8	"
	7	38	51	35	16.3	"
Comparative Example	1	35	56	85	12.5	Yes
	2	31	52	60	13.0	"
	3	29	49	50	12.0	"

Claims

1. A method of treating the surface of a water-absorbent resin, which comprises adding a hydrophilic crosslinking agent capable of reacting with at least two functional groups of the water-absorbent resin to